

# DIOXINS CONTAMINATION OF SEDIMENTS, FISH AND HUMAN ADIPOSE TISSUE IN THE NIIGATA PLAIN

Fukumura K<sup>1</sup>, Kajihara H<sup>2</sup>, Takahashi Y<sup>3</sup>

<sup>1</sup> Graduate School of Science and Technology, Niigata University, 2-8050 Ikarashi, Niigata City, 951-2181 Japan

<sup>2</sup> National Institute of Advanced Industrial Science and Technology

<sup>3</sup> Faculty of Engineering, Niigata University, 2-8050 Ikarashi, Niigata City, 951-2181 Japan

## Abstract

Dioxin concentration in lagoon sediments, fish, and human adipose tissues obtained in Niigata Prefecture; of Japan which is an area exposed to large amounts of sprayed herbicides were assessed. The toxic equivalent quantity (TEQ) value of the core sediment was higher than that investigated by the Ministry of the Environment, Japan. In our research, it has been predominantly focused on and contributed in the area of polychlorinated dibenzo-p-dioxins/polychlorinated dibenzofurans (PCDDs/PCDFs) and to a certain extent on the study of coplanar polychlorinated biphenyls (Co-PCBs). Principal component analysis and multiple liner regression analysis revealed that the contamination of dioxins in this core sediment mainly originated from the herbicides, Pentachlorophenol (PCP) and chloronitrophen (CNP), that were sprayed in the surrounding paddy fields. The TEQ values of the fish in this research were also higher than the national average in almost all the species investigated. The contribution of PCDDs/PCDFs to the total dioxin content was higher than the national average in all species. The herbicides used in this region (PCP and CNP) are considered to be the source of these dioxins. In contrast to the result of the core sediment, the Co-PCB concentration of the fish was very high. On the other hand the TEQ value and Co-PCB concentration in human adipose tissue of residents in a city in the prefecture were higher than the reported values. The ratio of PCDD/PCDF homologues differed, depending on the groups of the sample. However, there was almost no difference in the ratio of Co-PCB congeners. Thus, it was considered that dioxins in the living samples that were investigated result not only from exposure to herbicides but also to PCB.

## Introduction

The amount of dioxin (polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and dioxin-like PCBs (Co-PCBs)) produced during combustion and released as exhaust into the environment annually has decreased in Japan, particularly after the Law Concerning Special measures against dioxins was passed in 1999. However dioxins mainly accumulate in paddy field soils where the herbicides pentachlorophenol (PCP) and chloronitrophen (CNP) have been applied. These dioxins are present in the herbicides as byproducts. Niigata prefecture is one of the most famous regions for rice production in Japan, where a large amount of PCP and CNP have been used in the past. Therefore, it is considered that the dioxins may have moved into water systems from the paddy fields, subsequently contaminating fish in fresh and sea water, followed by gradual accumulation in the food chain. If this is true, it is possible that these compounds may have contaminated the human food chain. Thus, in this study, the dioxins in lagoon sediments, fish living in the lagoon and the coastal areas, and abdomen adipose tissues of residents in Niigata Prefecture were investigated, and to elucidate the relations between them was tried.

## Materials and Methods

### Materials

A sediment- core sample from Toyano Lagoon was obtained. This fresh water lagoon is in the lowest part of the Kameda-Gou region surrounded by the Shinano, Agano and Ko-Agano rivers (Figure 1). Paddy fields extent from the southern bank of the lagoon, and towns of Niigata City, from the northern bank. As a result, agricultural and urban effluents flow into the lagoon. It is consider that sediment contents of the lagoon reflect contamination by these effluents from this region. A core- sample of the sediment was taken for study of the time trend. Fish from the lagoon were also sampled to elucidate the dioxin transfer between the fish and the sediment. 3 kinds of fish, crucian carp, carp and black bass was taken to determine the differences among fish classes. Sea fish living

in the coastal zones of Niigata Prefecture were also taken. Further, human adipose tissues, gastrocolic omentum, a type of human adipose tissue were collected. The tissues were removed from the digestive apparatus of patients when they were operated in a hospital in the Shinano basin. The tissue collection was approved by the ethical committee of the School of Medicine of the Niigata University. Briefly, we tried to elucidate the dioxin behavior in the lower Shinano basin.

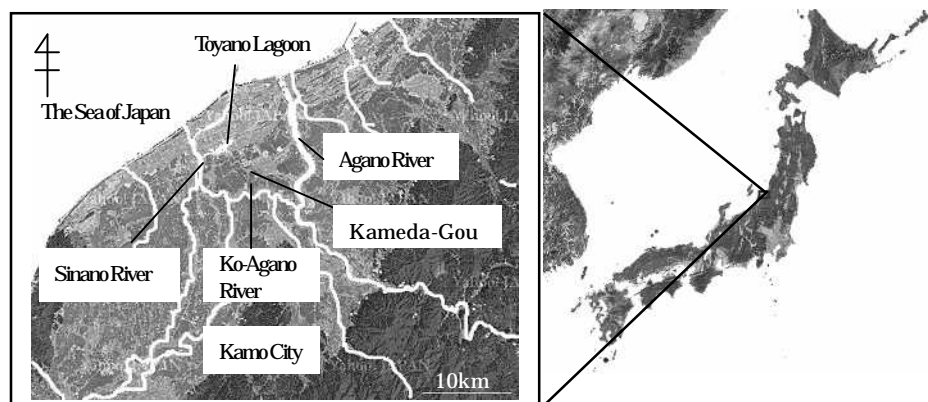


Figure 1 The locations of Niigata prefecture and the sampling point.

### Method

The sediment-core samples were vertically cut into 2-cm slices. A portion of a slice was used for dating using Pb-210 and Cs-137. The other portion of the slice was air dried at room temperature and pounded. The fish were cut and divided into muscle, viscera and bony parts. Muscle and viscera were used as analytical samples. They were homogenized, and freeze dried. The human adipose tissues were also freeze dried.

<sup>13</sup>C-labeled internal standards were added to the all the dried samples, which were then extracted by toluene using a Soxhlet apparatus. In the case of sediment samples, several small pieces of copper were added in a Soxhlet flask to remove the sulfur. Each of the fish and human sample extracts was divided between 10% and 90% in volume. The former was used for measuring fat content.

The latter was used for dioxin analysis. Each extract was concentrated using a rotary evaporator and treated several times with concentrated sulfuric acid. The extracts were then purified with hexane by a silica gel column followed by an active carbon-impregnated silica gel column. In the case of fish and human tissues, an alumina column was also used before the active carbon-impregnated silica gel column. The eluate, containing the final PCDD/PCDF and Co-PCB fractions, was concentrated and spiked with <sup>13</sup>C-labeled recovery standards. The 100- $\mu$ l condensates were injected into a high-resolution gas chromatography/mass spectrometry (HRGC-HRMS; Hewlett Packard HP6890/JEOL JMS 700) instrument.

### Results and Discussion

Figure 2 illustrates the temporal trend of the WHO1998-toxic equivalent quantity (TEQ) values in the sediment's core sample. In the 1946 slice (layer), the TEQ value was very small, and it increased gradually and approached a peak in 1968. This value subsequently decreased annually, and it has plateaued in recent years. When compared with the results of the Tokyo bay, and the Kasumigaura, and Haruna lakes<sup>1)</sup>, the TEQ value of the Toyano Lagoon was higher.

The TEQ value of PCDDs accounts for

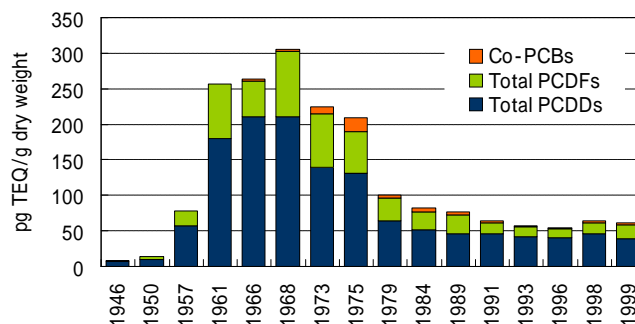


Figure 2 The TEQ value in the core sediment of Toyano Lagoon.

60-80% of the total annual TEQ value. In contrast, that of Co-PCBs represented only 0.32-6.1% of the annual TEQ value. Results of principal component analysis and multiple linear regression analysis, revealed that most of the dioxins found in Toyano Lagoon originated from PCP and CNP<sup>2)</sup>. In addition, the time trend of the congeners that were contained PCP and CNP was in good accordance with that of the applied amounts of PCP and CNP. Therefore, we concluded that the sediments from Toyano Lagoon are mainly contaminated by PCP and CNP in Kameda-Gou.

Figure 3 illustrates TEQ values of the fish obtained from Toyano Lagoon (left) and the nation-wide average TEQ values (right)<sup>3)</sup>. The TEQ values of fish are based on the wet weight of the muscles. The average value of crucian carp, carp and black bass in the Toyano Lagoon were 2.8, 2.1, and 5.6 pg TEQ/g- wet weight, respectively. The amounts of dioxins in the fish of Toyano Lagoon were higher than the nation-wide average in all fish species.

In addition, the percentages of PCDD/PCDF in TEQ were higher than those of the nation-wide average for all the species investigated. The percentage of Co-PCB in Toyano Lagoon fish was found to be higher as compared to that in the sediment core samples.

Figure 4 illustrates the result of the fish living in the coastal areas of Niigata prefecture. The TEQ value of *Trachurus japonicus* was 1.1 pg TEQ/g-wet weight and it was the lowest among all the species. The TEQ value of *Sardinops melanostictus* was 4.1 pg TEQ/g-wet weight, and it was the highest among all the species. The TEQ values were higher than those of the nation-wide average<sup>3)</sup> in all species except *Konosirus punctatus*. The percentage of Co-PCB tended to be higher in bigger fishes except for *Sardinops melanostictus*.

There were similarities between the fish in Toyano Lagoon and those in the coastal area of Niigata prefecture, i.e. the TEQ values and percentages of PCDD/PCDF were higher than those of the nation-wide average.

Figure 5 illustrates the results of human adipose tissue (n = 42, average age, 72 years). The TEQ value of this study was higher than results of Takenaka et al<sup>4)</sup> (n = 21, average age, 63 years) and the Ministry of the Environment<sup>5)</sup> (n = 21, average age, 47 years). However the percentage of PCDD/PCDF was lower, this was the point of difference between result of human adipose tissue and those of fish. It was suggested that the high percentage of Co-PCBs was a result of the high average age of subjects. Further the TEQ values tended to be higher in female (n = 21, average age, 74 years) than in males (n = 21, average age, 70 years).

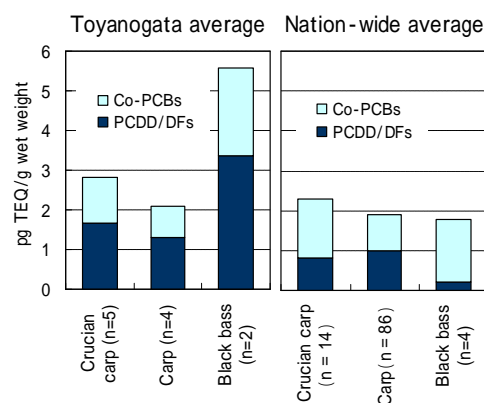


Figure 3 Comparison between the TEQ values of Toyano lagoon fish (left) and those of the nation-wide average (right).

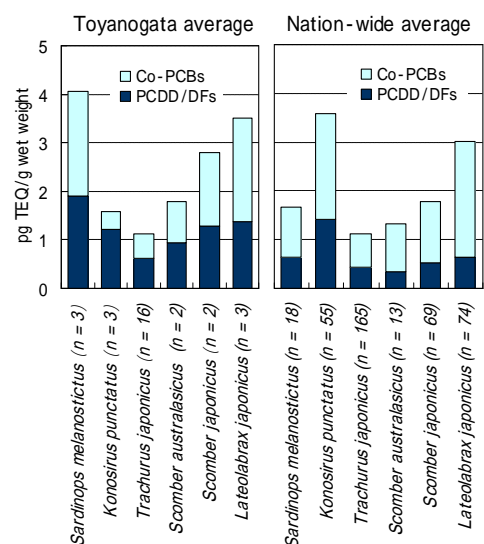


Figure 4 Comparison between the TEQ values of the fish in coastal areas of Niigata (left) and those of nation-wide average (right).

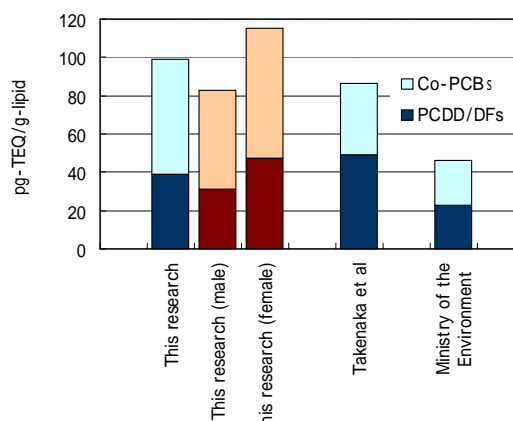


Figure 5 Comparison of the TEQ values in human adipose tissue obtained in this and other investigations.

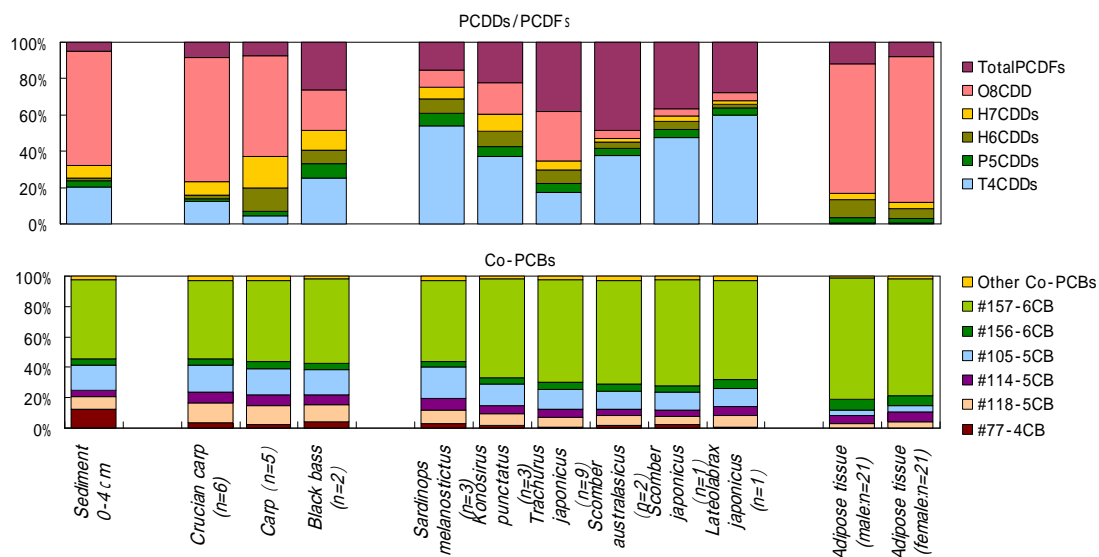


Figure 6 Percentage of homologues in total PCDD/PCDF (upper figure) and the congeners in the total Co-PCB (lower figure).

Figure 6 illustrates the percentages of each homologue in the total PCDD/PCDF and those of Co-PCBs in the abovementioned samples. The ratio of O8CDD in the crucian carp and carp was predominant and that of PCDFs was low. These results are similar to those obtained with sediment samples. However, the ratios of O8CDD and PCDF in black bass differed from the abovementioned values. The ratio of T4CDDs and PCDF is predominant in the fish living in the coastal area of Niigata prefecture. The percentage of T4CDDs tended to be larger in bigger fish. O8CDD was predominant in the human adipose tissue, and no difference was observed between males and females. As for Co-PCB, the percentage of 157-6CB was the highest in all the samples.

## References

1. Ministry of the Environment of Japan (1998)  
[http://www.env.go.jp/info/iken/h140610a/sanko\\_16.html](http://www.env.go.jp/info/iken/h140610a/sanko_16.html)
2. Mizuki Sakai, Hideo Kajihara, Kinumi Fukumura, Jun Kobayashi, Manabu Ohizumi, Yukio Takahashi, Hiroto Nakadaira and Masaharu Yamamoto (2001) Time trend and source for dioxins in sediments in a large-scale rice production area, Niigata, Japan. *Organohalogen Compounds* 57, 11-14
3. Ministry of the Environment of Japan (1999)  
[http://www.env.go.jp/press/file\\_view.php?serial=1004&hou\\_id=1486](http://www.env.go.jp/press/file_view.php?serial=1004&hou_id=1486)
4. Shigeyuki Takenaka, Takashi Todaka, Matayoshi Nakamura, Tsuguhide Hori, Takao Iida, Taketo Yamada, Jun-ichi Hata (2002) Polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans and non-ortho, mono-ortho chlorine substituted biphenyls in Japanese human liver and adipose tissue. *Chemosphere* 49, 161-172
5. Ministry of the Environment of Japan (1997)  
<http://www.env.go.jp/houdou/gazou/1837/1318/389.pdf>